Delicate, a study of structural change in ten-coordinated La(III), Ce(III), Pr(III), Nd(III), Sm(III) and Eu(III) sulfates

Supporting Information

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Contents

1. Crystals

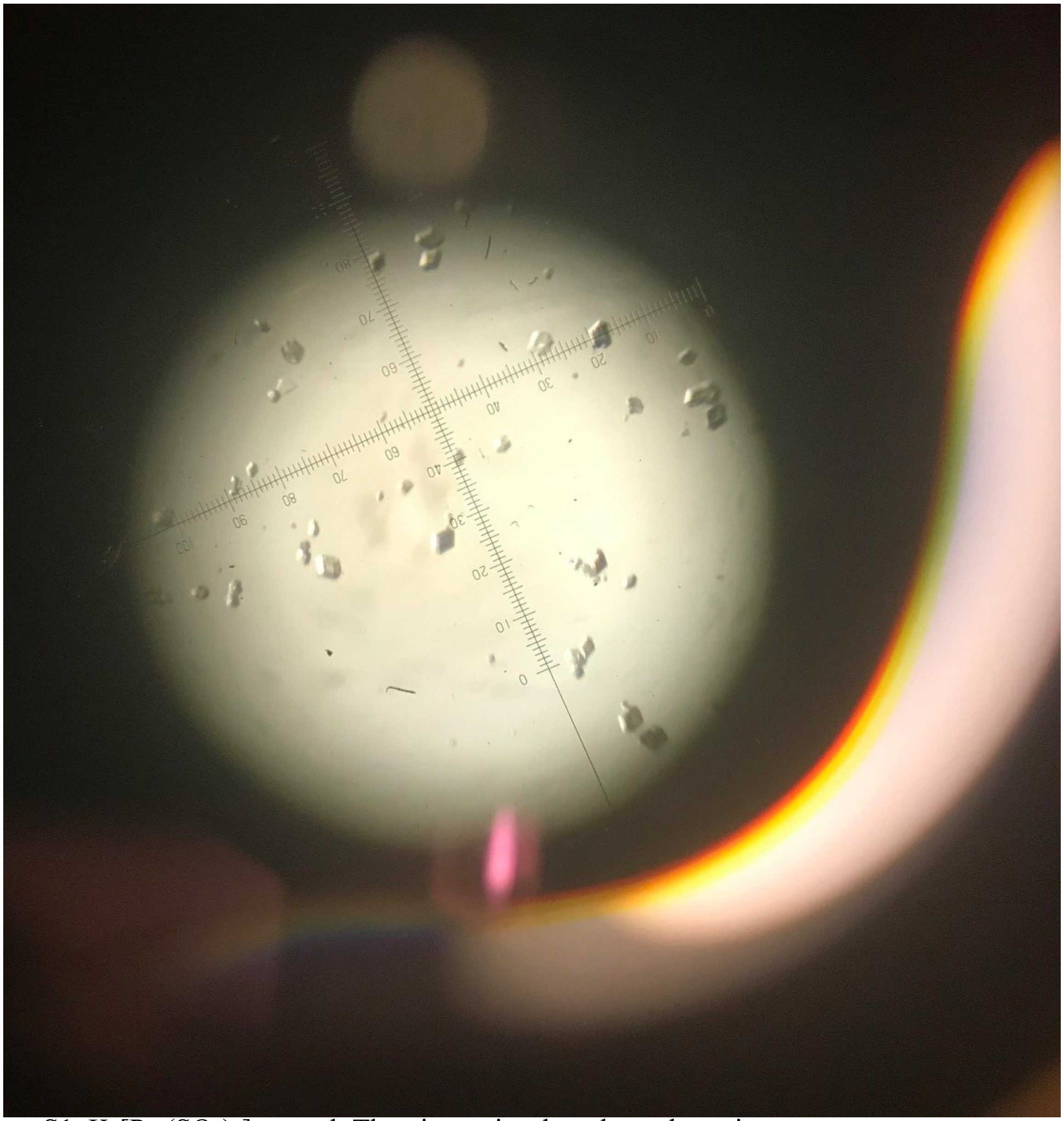


Figure S1. $K_6[Pr_2(SO_4)_6]$ crystal. The picture is taken through a microscope.

2. Crystallographic Information

The crystals $K_5Na[Ce_2(SO_4)_6]$ (ICSD: 281576) and $K_5Na[Eu_2(SO_4)_6]$ (CCDC: 2070452) were published elsewhere.[1,2]

Empirical formula	$La_2K_6O_{24}S_6$	$Ce_2K_6O_{24}S_6$	$Pr_2K_6O_{24}S_6$	$Nd_2K_5NaO_{24}S_6$	$Sm_2K_5NaO_{24}S_6$
Formula weight	1088.78	1091.20	1092.78	1083.33	1095.55
Temperature/K	100	100	100	100	100
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/m	C2/m	C2/m	C2/m	C2/m
a/Å	9.2182(6)	9.1884(7)	9.168 (3)	9.1404 (6)	9.1152 (6)
b/Å	16.3683(9)	16.3639(13)	16.317 (5)	16.2841 (11)	16.1688 (10)
c/Å	7.7108(4)	7.6768(6)	7.651 (2)	7.6453 (5)	7.6393 (4)
β/°	111.243(2)	111.324(3)	111.04 (3)	110.991 (2)	110.639 (2)
Volume/Å^3	1084.40(11)	1075.25(15)	1071.4 (2)	1062.43 (12)	1053.63 (11)
Z	2	2	2	2	2
ρ_{calc}g/cm^3	3.334	3.370	3.398	3.386	3.453
μ/mm^{-1}	5.731	6.040	6.379	6.539	7.239
F(000)	1032.0	1036.0	1040.0	1028.0	1036.0
Crystal size/mm^3	0.165 × 0.151 × 0.094	0.196 × 0.175 × 0.078	0.238 × 0.212 × 0.07	0.188 × 0.096 × 0.082	0.116 × 0.087 × 0.068
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.978 to 71.258	4.978 to 54.96	4.992 to 72.83	5.004 to 72.624	5.038 to 72.63
Index ranges	$-15 \le h \le 15$, $-26 \le k \le 26$, $-12 \le l \le 12$	$-11 \le h \le 9$, $-21 \le k \le 21$, $-9 \le l \le 9$	$-15 \le h \le 15$, $-27 \le k \le 27$, $-12 \le l \le 12$	$-15 \le h \le 11$, $-27 \le k \le 27$, $-12 \le l \le 12$	$-15 \le h \le 15$, $-26 \le k \le 25$, $-11 \le l \le 12$
Reflections collected	21705	13325	16671	21714	21452
Independent reflections	2580 [R_{int} = 0.0326, R_{sigma} = 0.0181]	1277 [R_{int} = 0.0591, R_{sigma} = 0.0266]	2678 [R_{int} = 0.0444, R_{sigma} = 0.0287]	2653 [R_{int} = 0.0509, R_{sigma} = 0.0289]	2632 [R_{int} = 0.0653, R_{sigma} = 0.0347]
Data/restraints/parameters	2580/0/95	1277/0/102	2678/0/102	2653/0/102	2632/0/95
Goodness-of-fit on F^2	1.144	1.135	1.122	1.099	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0226, wR_2 = 0.0652	R_1 = 0.0250, wR_2 = 0.0702	R_1 = 0.0233, wR_2 = 0.0628	R_1 = 0.0265, wR_2 = 0.0650	R_1 = 0.0202, wR_2 = 0.0475
Final R indexes [all data]	R_1 = 0.0252, wR_2 = 0.0664	R_1 = 0.0266, wR_2 = 0.0708	R_1 = 0.0265, wR_2 = 0.0639	R_1 = 0.0319, wR_2 = 0.0672	R_1 = 0.0250, wR_2 = 0.0489
Largest diff. peak/hole / e Å^{-3}	2.63/-3.36	0.84/-1.11	2.01/-2.16	5.44/-1.97	0.94/-1.29

CCDC numbers:

$K_6[La_2(SO_4)_6]$: 2142173, $K_6[Ce_2(SO_4)_6]$: 2150608, $K_6[Pr_2(SO_4)_6]$: 2142174, $K_5Na[Nd_2(SO_4)_6]$: 2142177, $K_5Na[Sm_2(SO_4)_6]$: 2142178

3. Powder X-ray Diffractogram

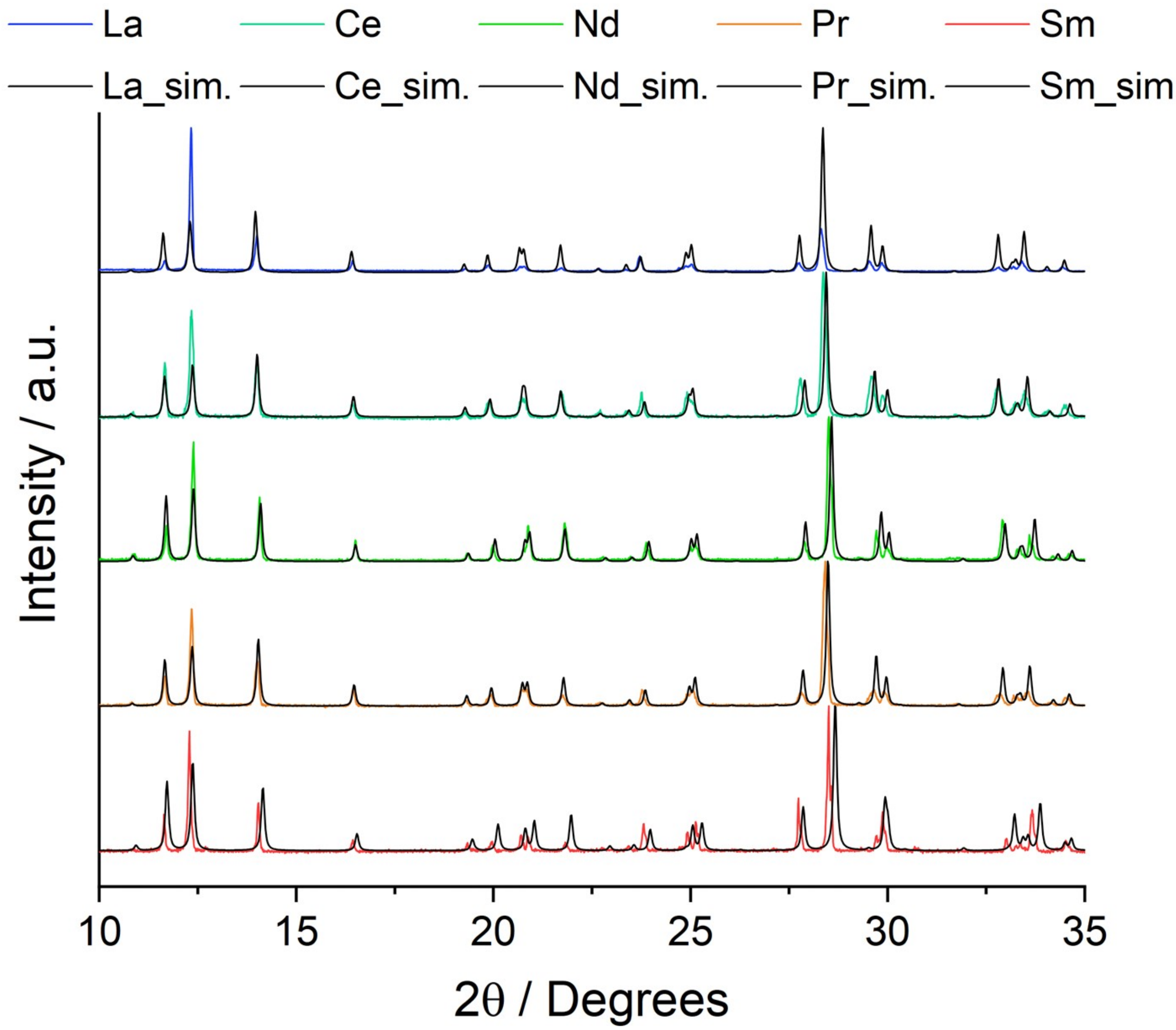


Figure S2. Powder X-ray diffractograms of $K_6Na[Ln_2(SO_4)_6]$ (Ln = La, Ce, Pr) and $K_5Na[Ln_2(SO_4)_6]$ (Ln = Nd, Sm)

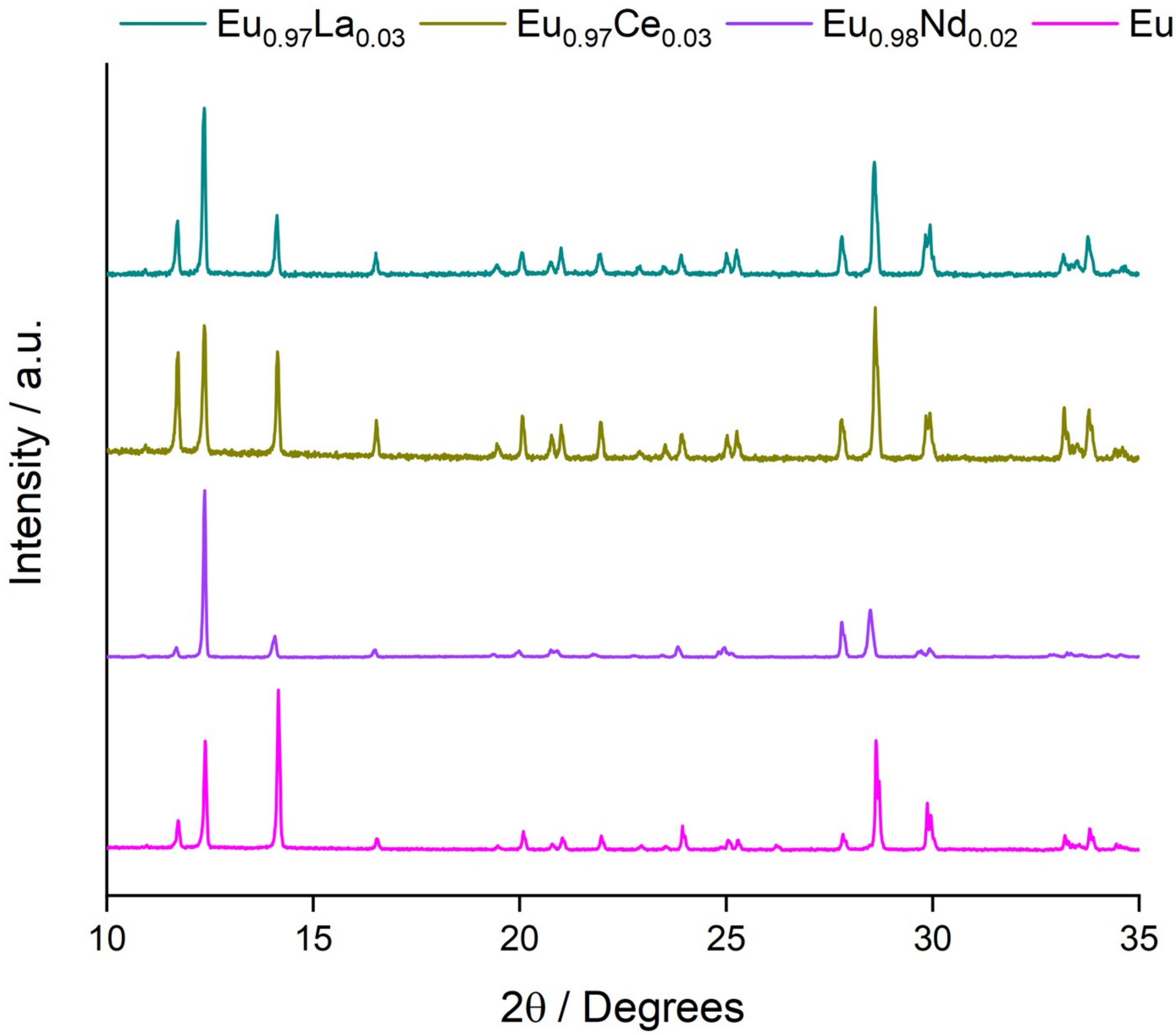


Figure S3. Powder X-ray diffractograms of $K_5Na[(Eu_{0.97}La_{0.03})_2(SO_4)_6]$, $K_5Na[(Eu_{0.97}Ce_{0.03})_2(SO_4)_6]$, $K_5Na[(Eu_{0.98}Nd_{0.02})_2(SO_4)_6]$ and $K_5Na[Eu_2(SO_4)_6]$.

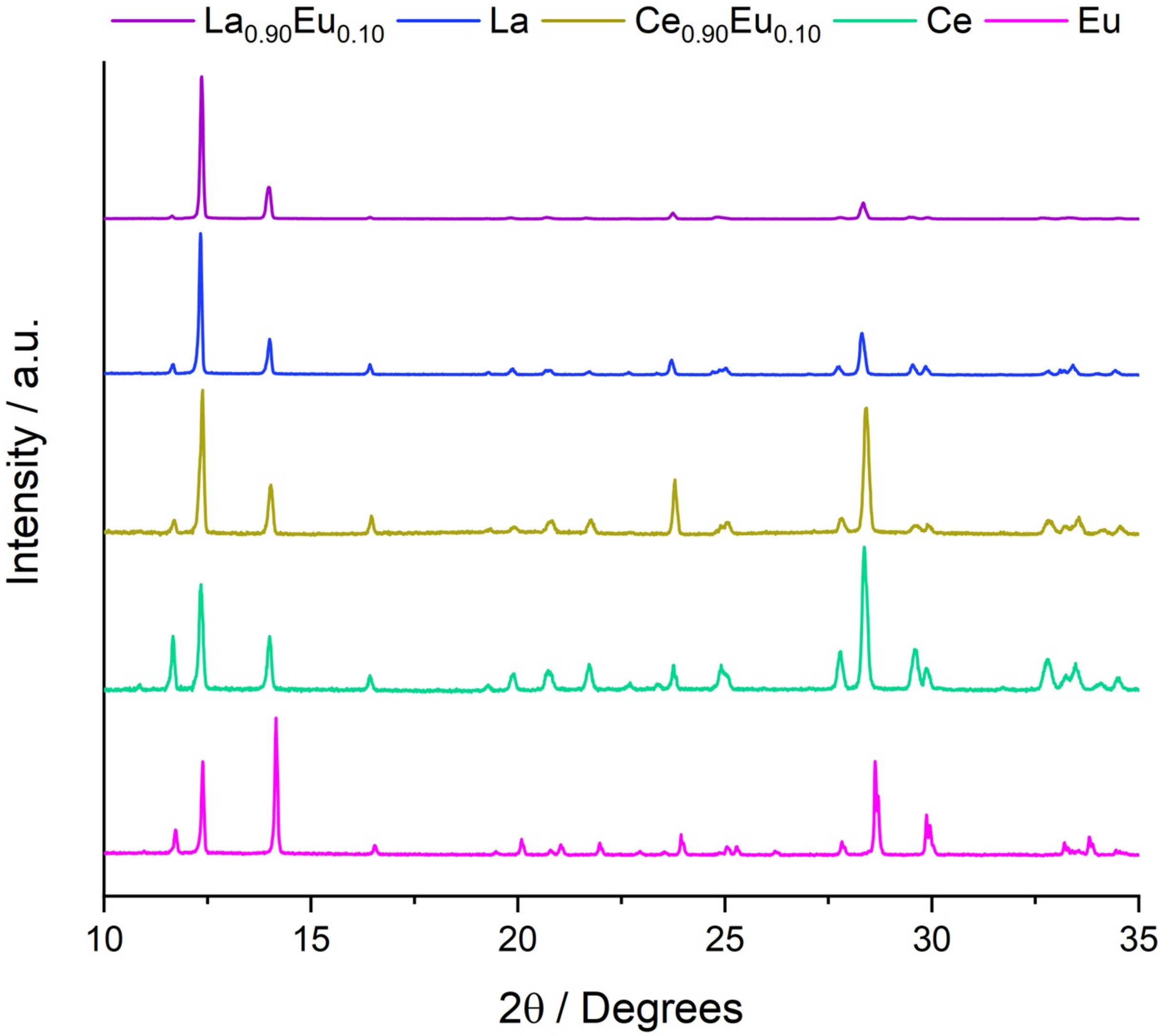


Figure S4. . Powder X-ray diffractograms of, $K_6[(La_{0.90}Eu_{0.10})_2(SO_4)_6]$, $K_6[La_2(SO_4)_6]$, $K_6[(Ce_{0.90}Eu_{0.10})_2(SO_4)_6]$, $K_6Ce_2(SO_4)_6]$ and $K_5Na[Eu_2(SO_4)_6]$.

4. X-ray fluorescence spectroscopy

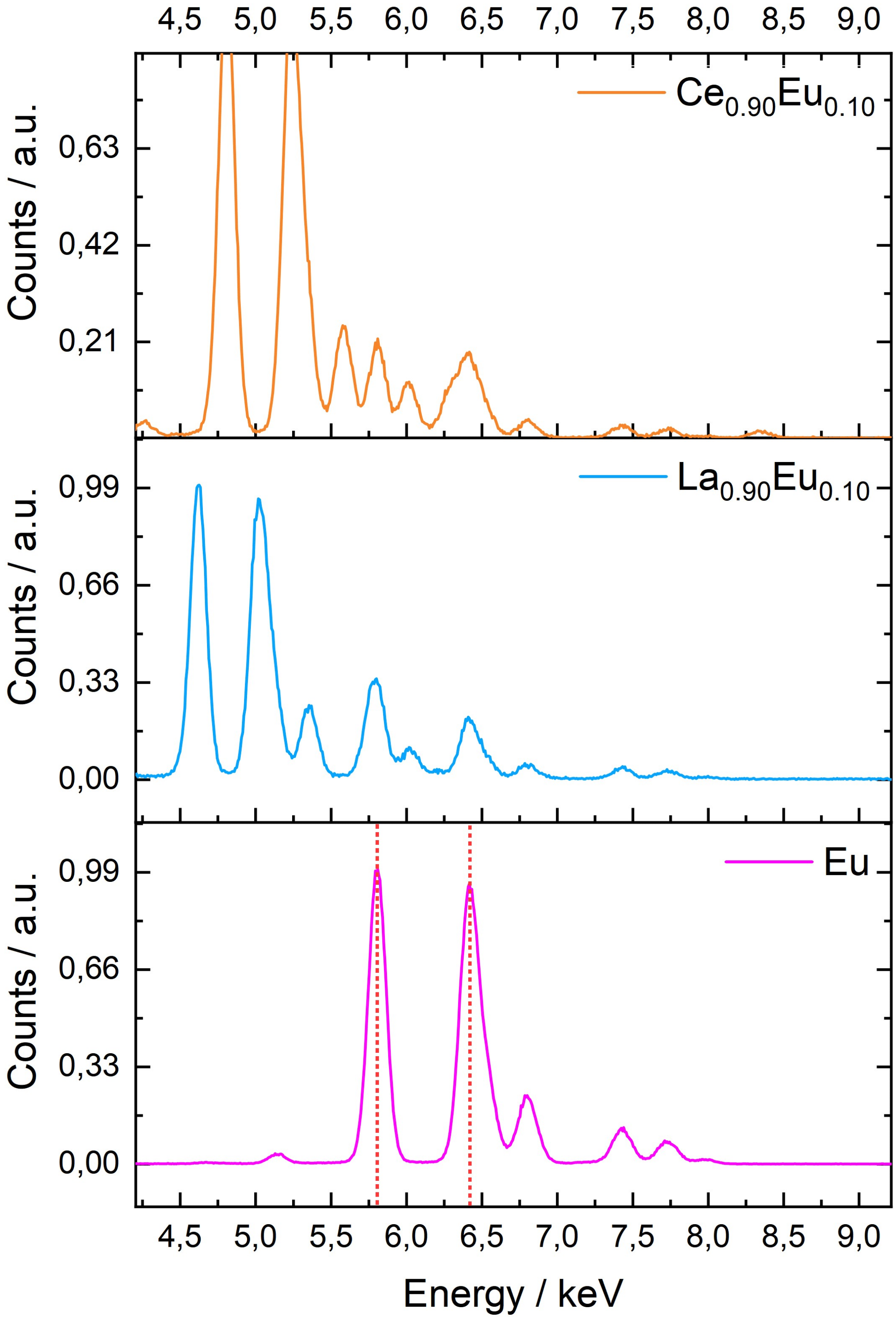


Figure S5. X-ray fluorescence spectrum of $K_6[(La_{0.90}Eu_{0.10})_2(SO_4)_6]$, $K_6[(Ce_{0.90}Eu_{0.10})_2(SO_4)_6]$, and $K_5Na[Eu_2(SO_4)_6]$ powders.

5. Time-resolved emission decay profiles

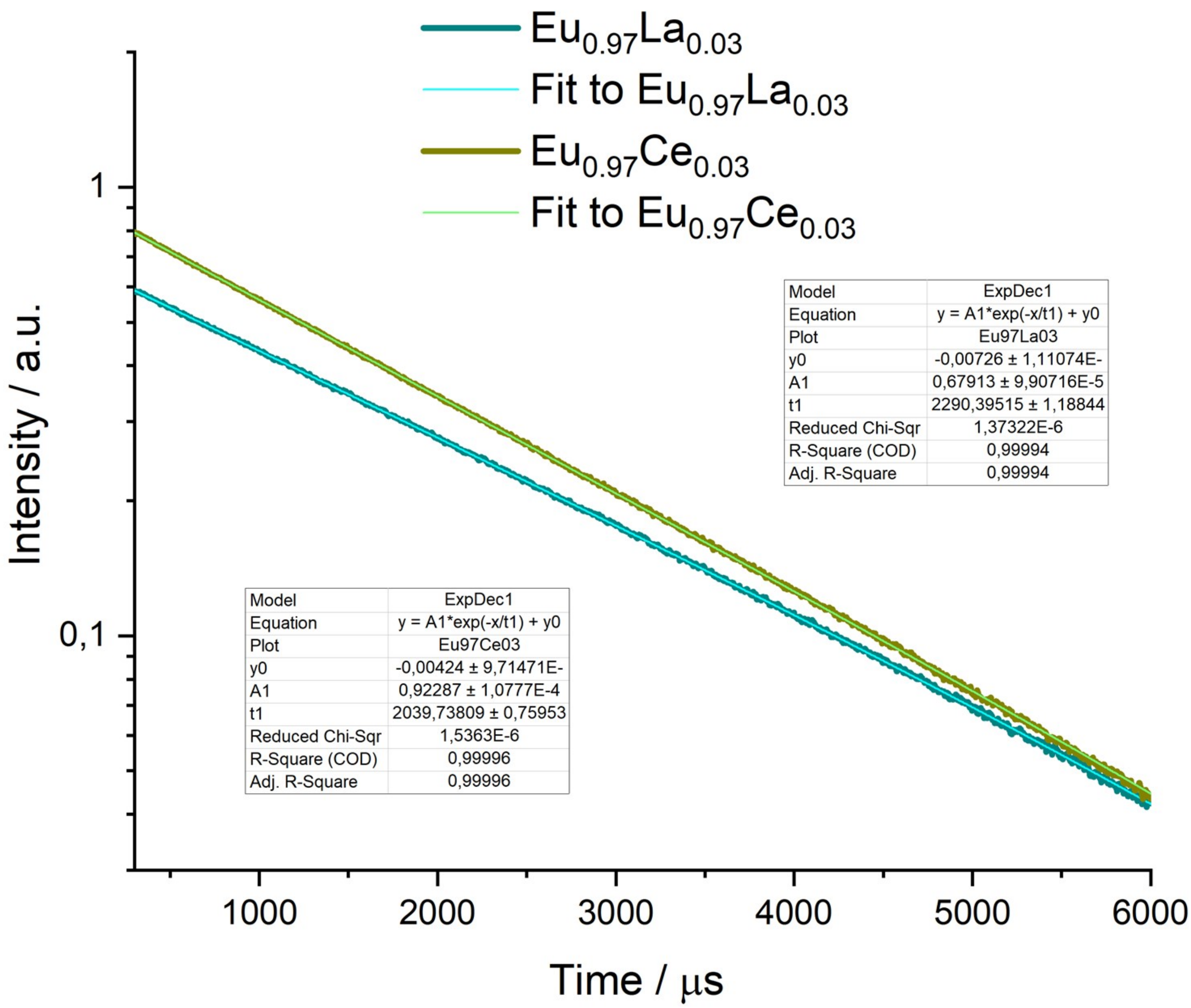


Figure S6. Time resolved decay profiles of $K_5Na[(Eu_{0.97}La_{0.03})_2(SO_4)_6]$ and $K_5Na[(Eu_{0.97}Ce_{0.03})_2(SO_4)_6]$ powders recorded in dimethyl tetrahydrofuran glass at 77K.

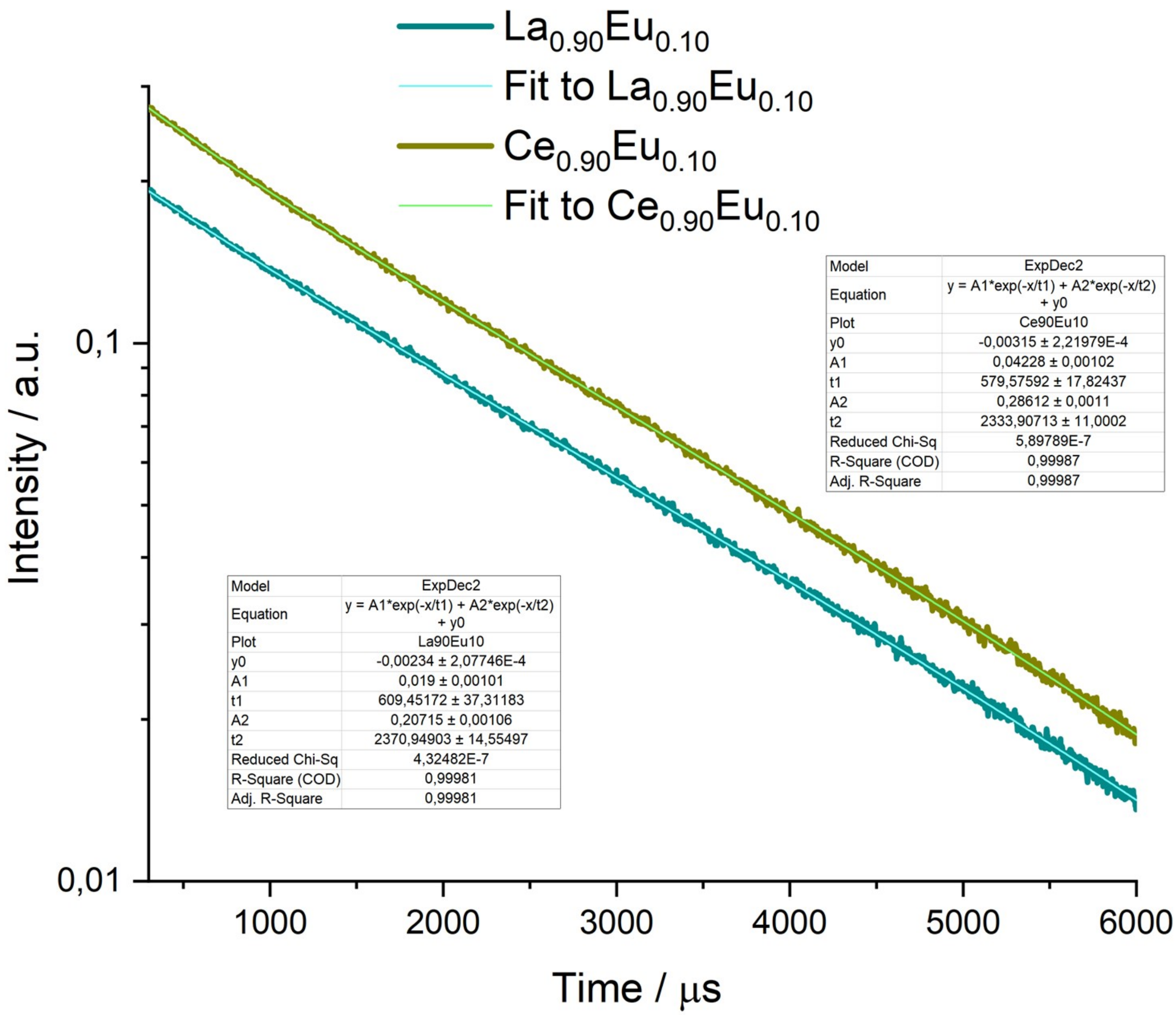


Figure S7. Time resolved decay profiles of $K_6[(La_{0.90}Eu_{0.10})_2(SO_4)_6]$ and $K_6[(Ce_{0.90}Eu_{0.10})_2(SO_4)_6]$ powders recorded in dimethyl tetrahydrofuran glass at 77K.

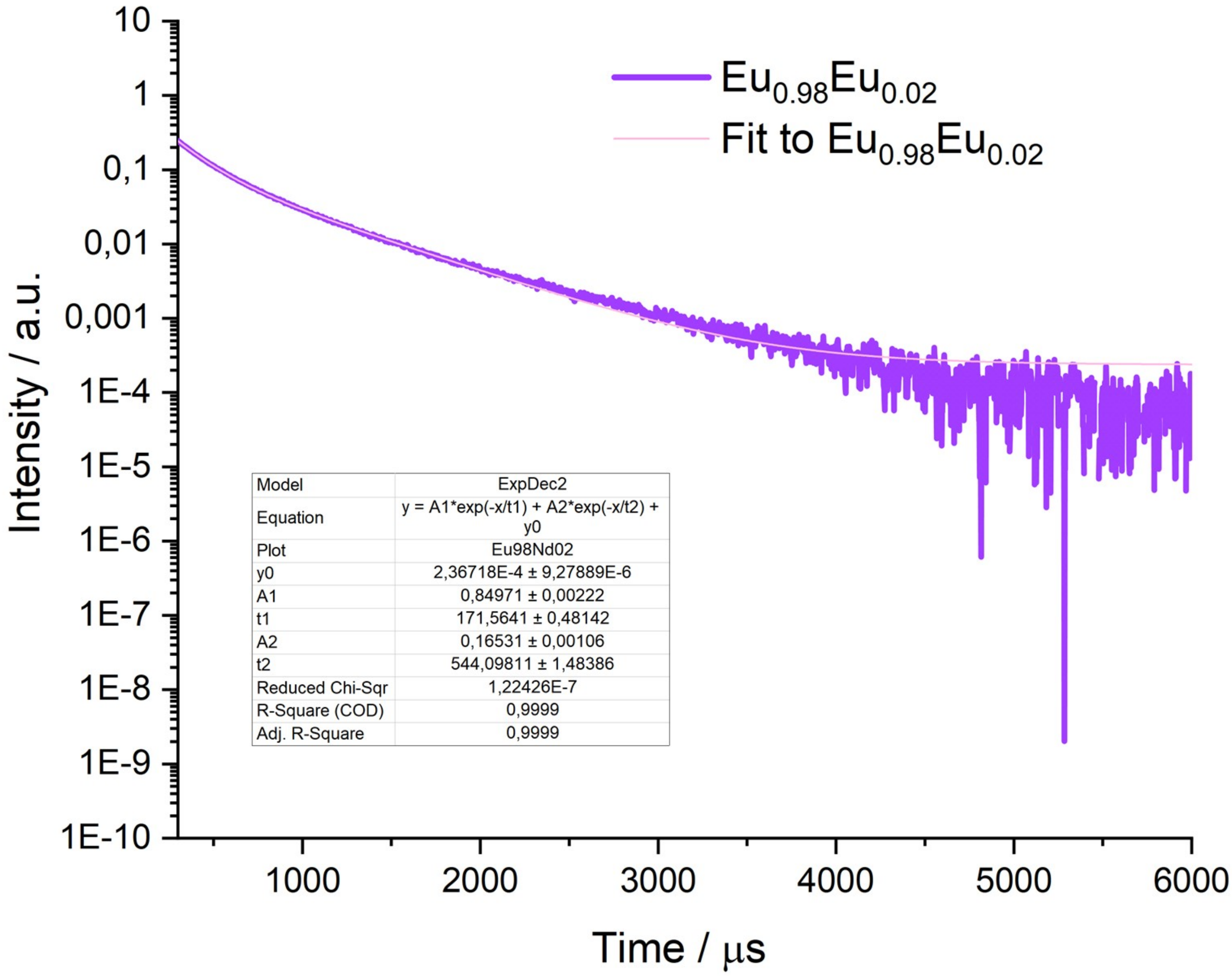


Figure S8. Time resolved decay profiles of $K_5Na[(Eu_{0.98}Nd_{0.02})_2(SO_4)_6]$ powders recorded in dimethyl tetrahydrofuran glass at 77K.

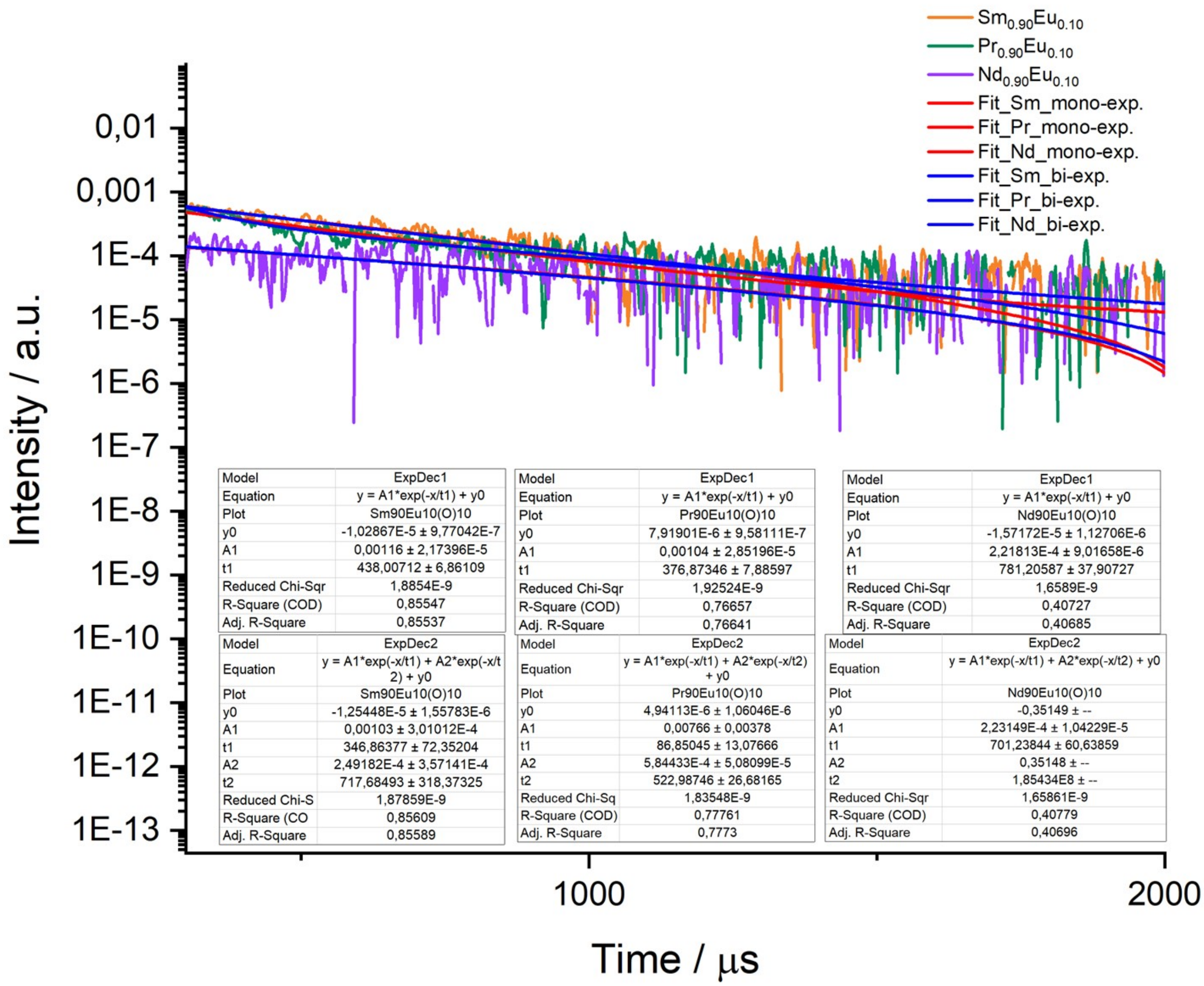


Figure S9. Time resolved decay profiles of $K_5Na[(Sm_{0.90}Eu_{0.10})_2(SO_4)_6]$, $K_5Na[(Pr_{0.90}Eu_{0.10})_2(SO_4)_6]$ and $K_5Na[(Nd_{0.90}Eu_{0.10})_2(SO_4)_6]$ powders recorded in dimethyl tetrahydrofuran glass at 77K.

6. Excitation spectra

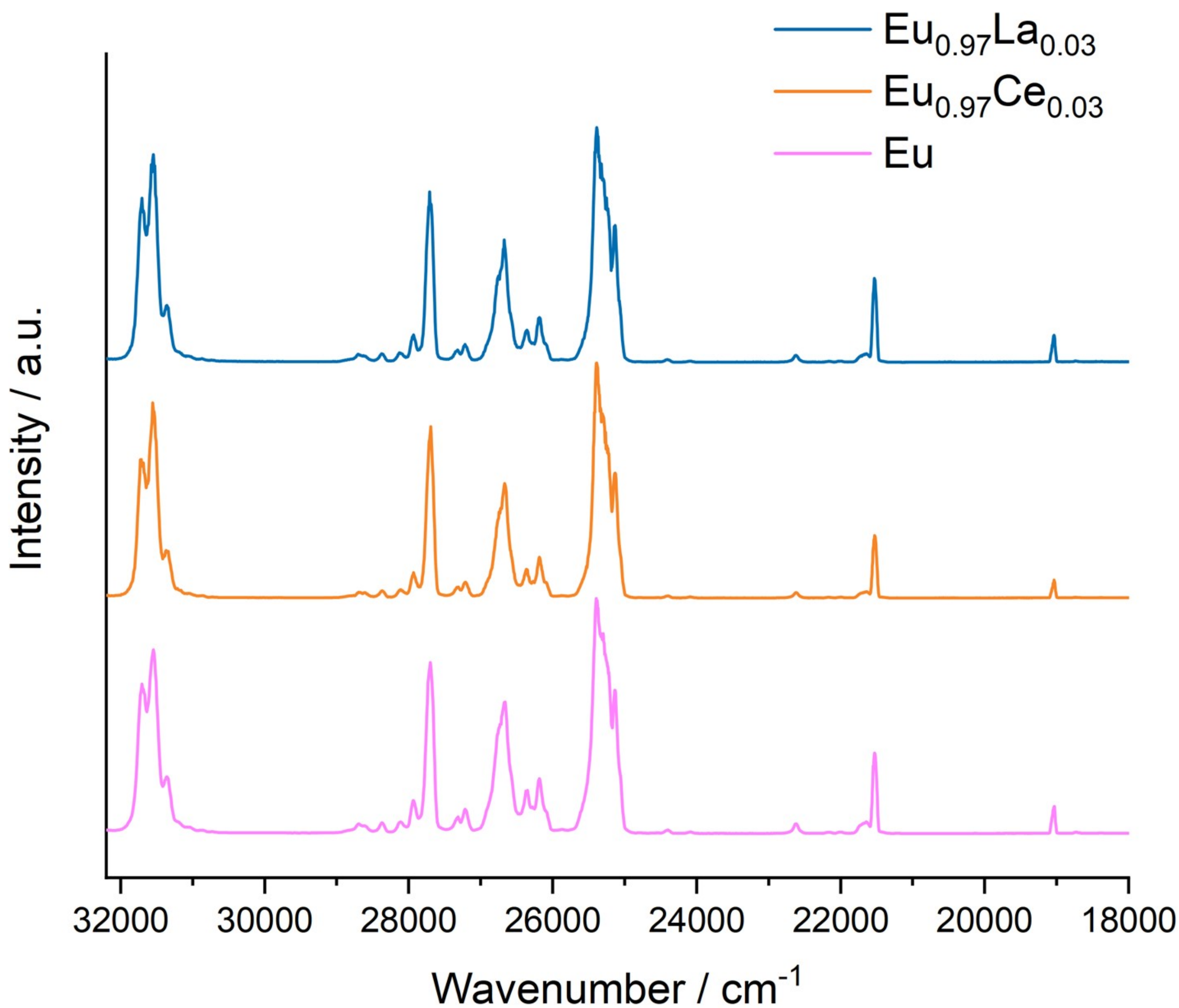


Figure S10. Normalized excitation spectra (em. 614 nm) of $K_5Na[(Eu_{0.97}La_{0.03})_2(SO_4)_6]$ $K_5Na[(Eu_{0.97}Ce_{0.03})_2(SO_4)_6]$ and $K_5Na[Eu_2(SO_4)_6]$ powders in dimethyl tetrahydrofuran glass at 77K. Excitation slit = 1, 1.5, 1 nm.

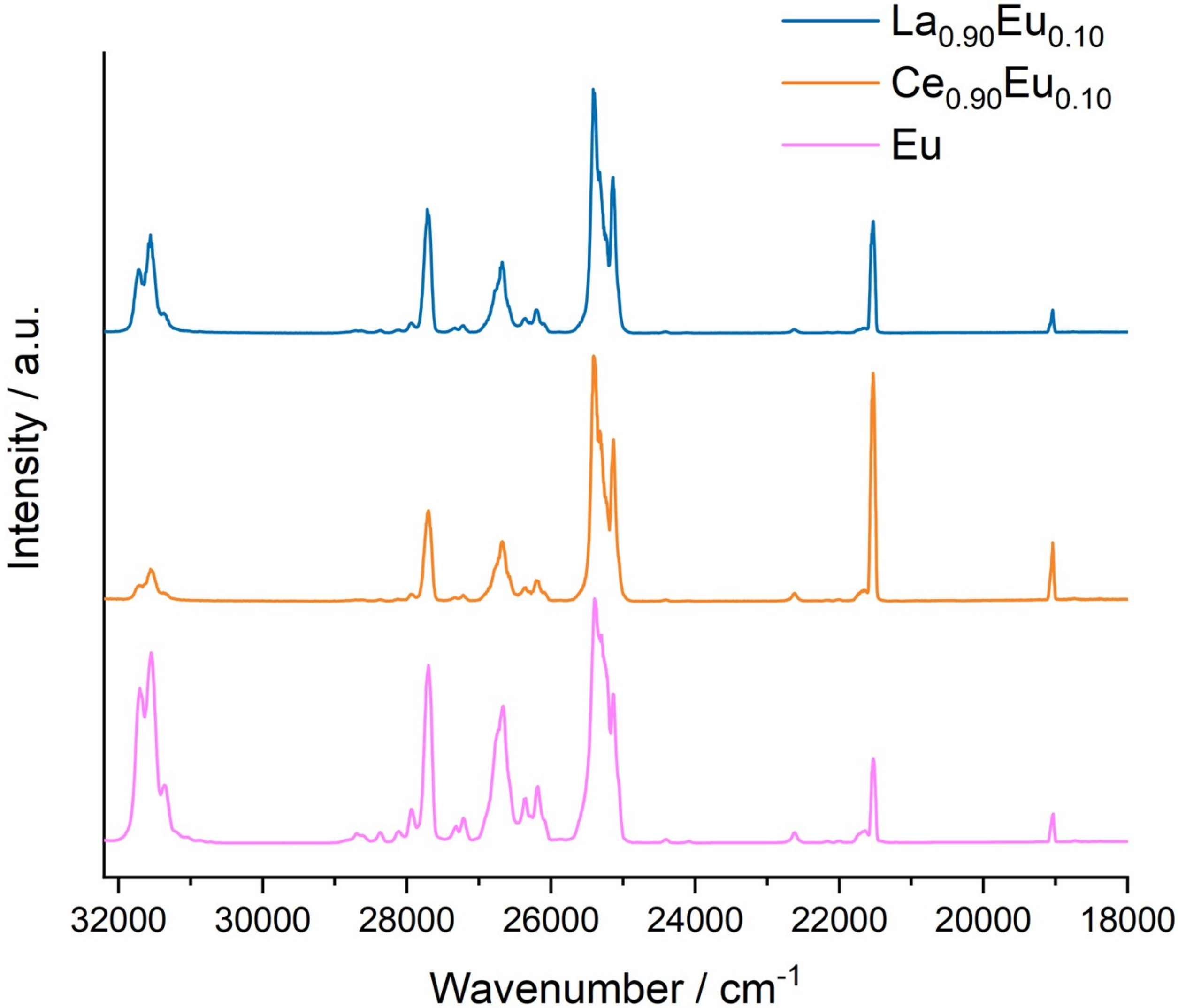


Figure S11. Normalized excitation spectra (em. 614 nm) of $K_6[(La_{0.90}Eu_{0.10})_2(SO_4)_6]$ $K_6[(Ce_{0.90}Eu_{0.10})_2(SO_4)_6]$ and $K_5Na[Eu_2(SO_4)_6]$ powders in dimethyl tetrahydrofuran glass at 77K. Excitation slit = 1, 1.5, 1 nm.

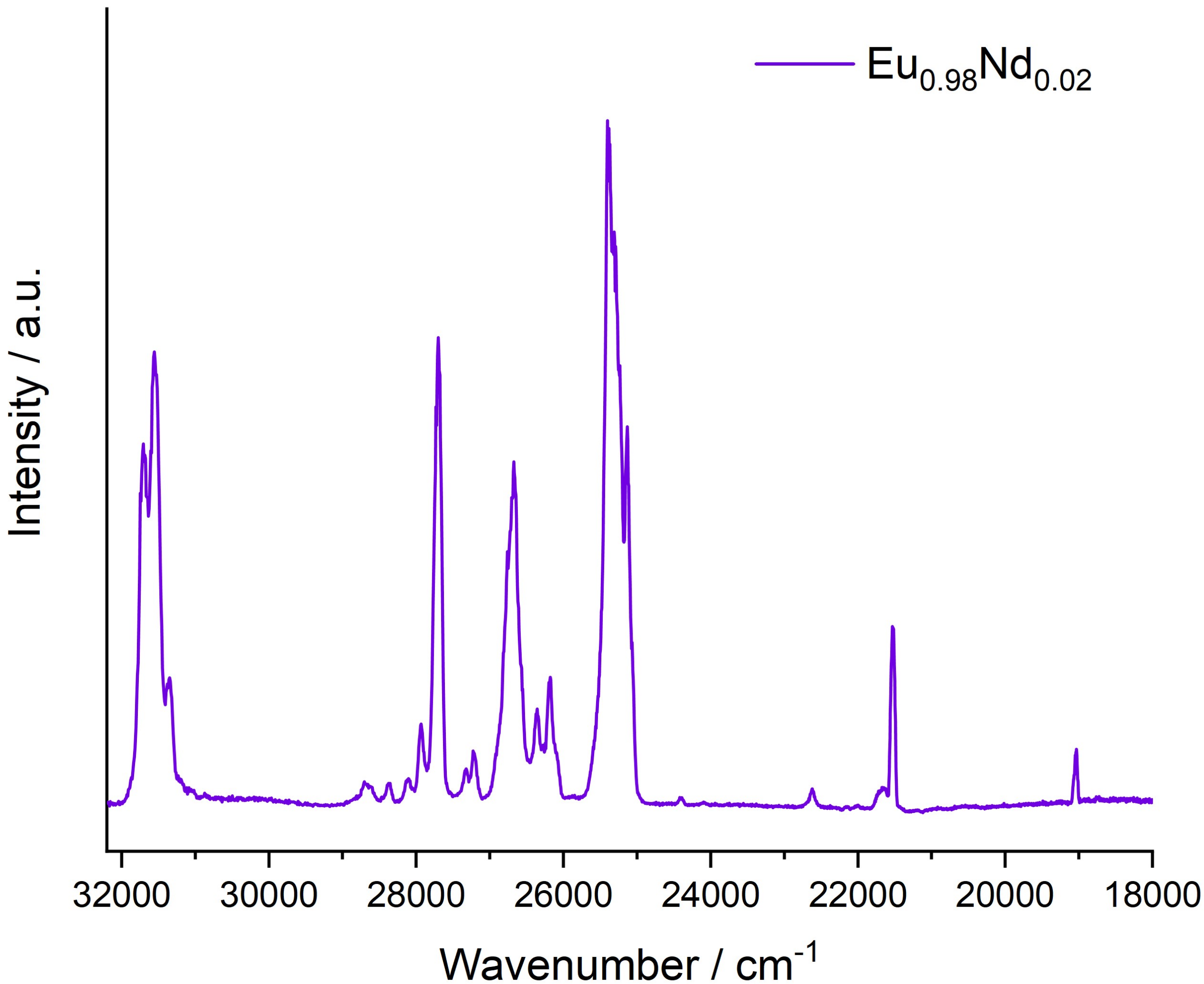


Figure S12. Normalized excitation spectra (em. 614 nm) of $K_5Na[(Eu_{0.98}Nd_{0.02})_2(SO_4)_6]$ powders in dimethyl tetrahydrofuran glass at 77K. Excitation slit = 1, 1.5, 1 nm.

7. Emission spectrum $K_5Na[(Eu_{0.98}Nd_{0.02})_2(SO_4)_6]$ – Long range

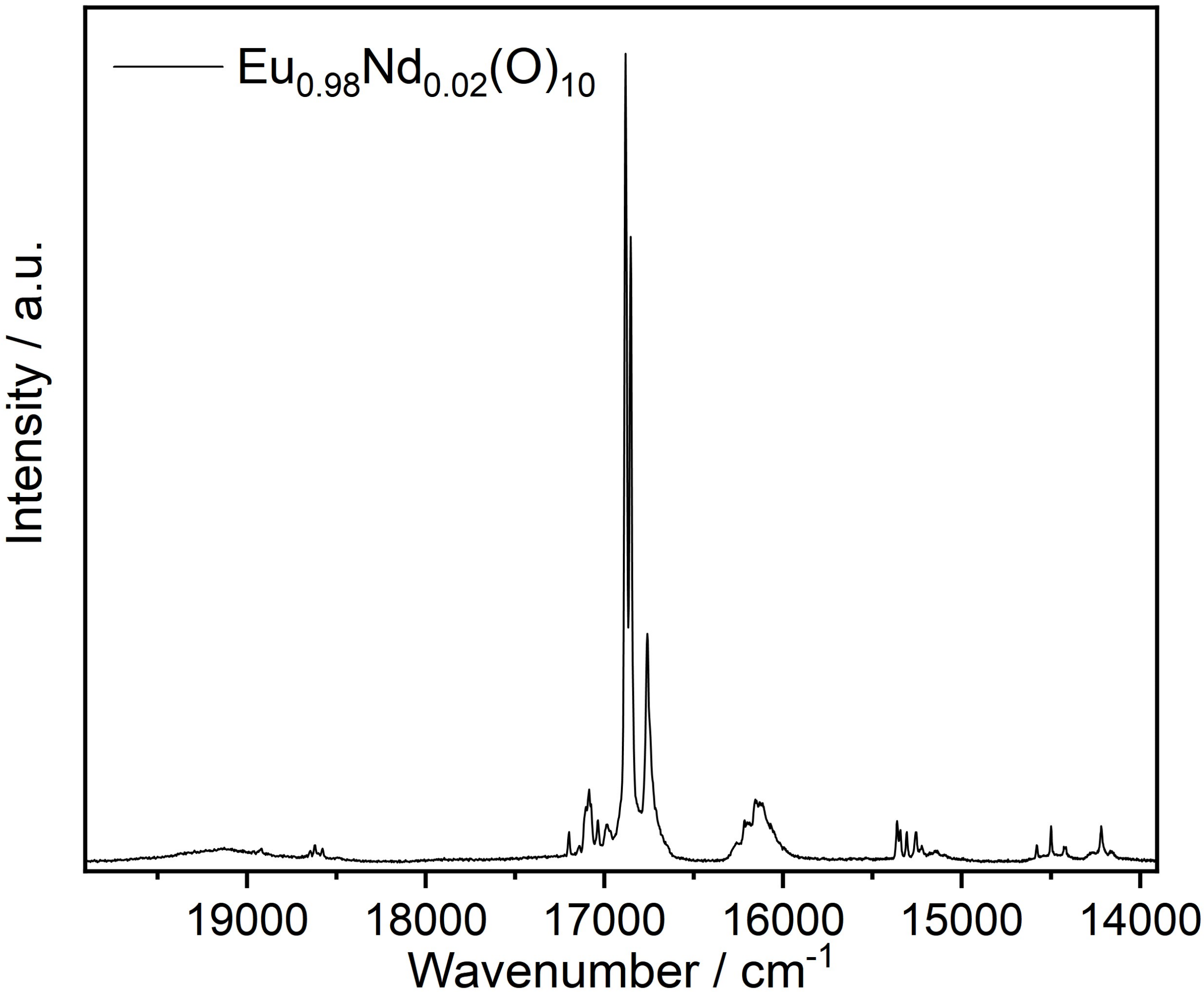


Figure S13. Emission spectrum $K_5Na[(Eu_{0.98}Nd_{0.02})_2(SO_4)_6]$ powder in dimethyl tetrahydrofuran glass at 77K. Excitation slit = 1.0 nm.

8. Gaussian fits of the $^7F_1$ transition band

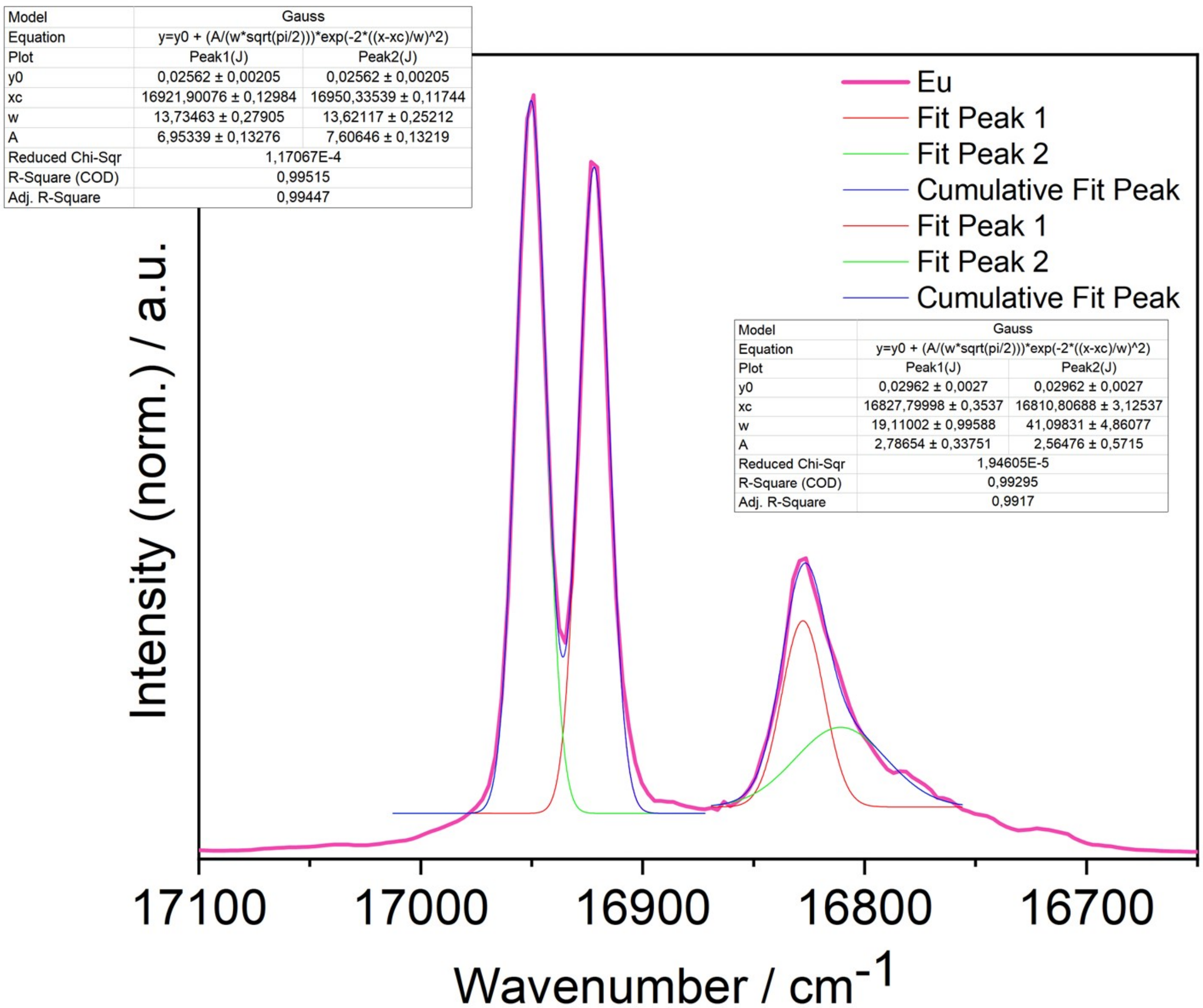


Figure S14. Gaussian fits of the $^7F_1$ transition band in $K_5Na[(Eu)_2(SO_4)_6]$.

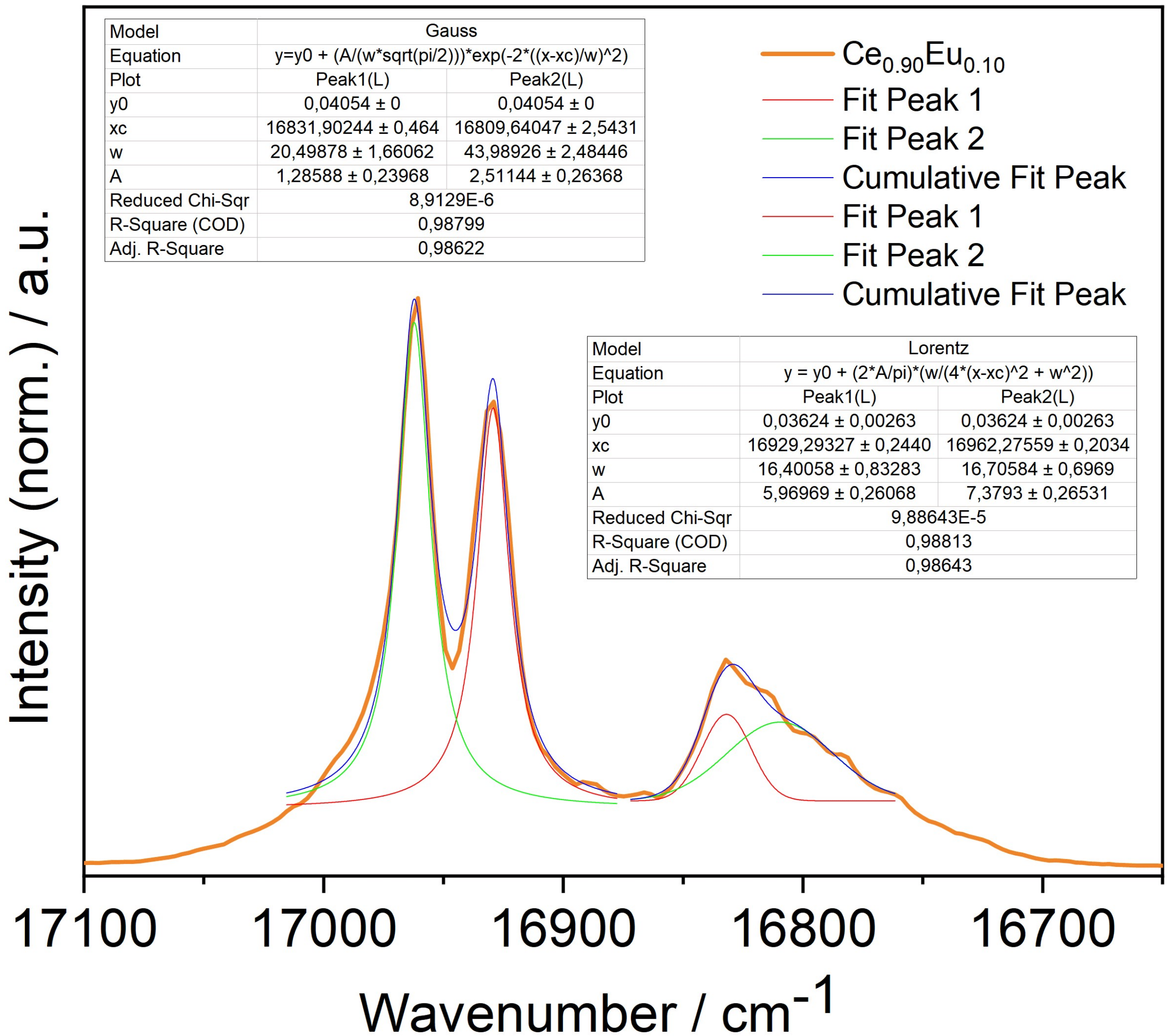


Figure S15. Gaussian fits of the $^7F_1$ transition band in $K_6[(Ce_{0.90}Eu_{0.10})_2(SO_4)_6]$.

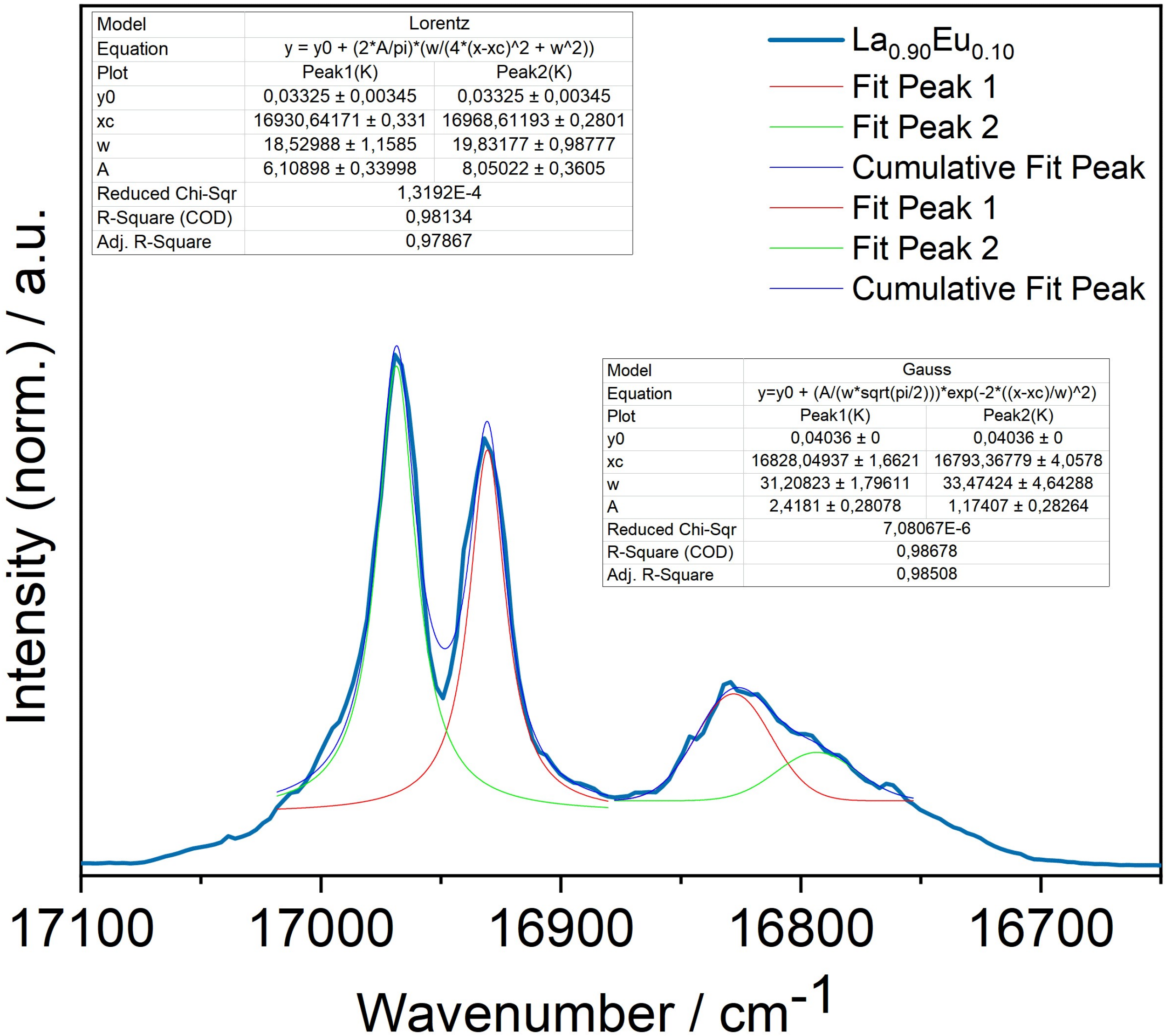


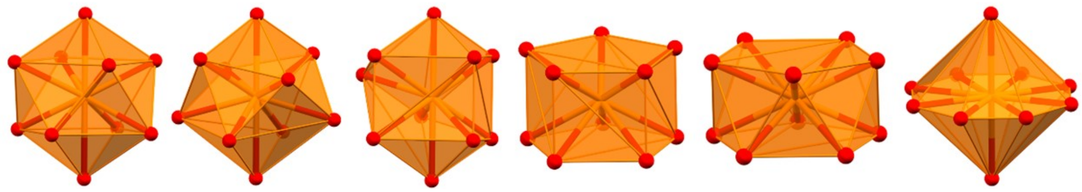
Figure S16. Gaussian fits of the $^{7}F_{1}$ transition band in $K_6[(La_{0.90}Eu_{0.10})_2(SO_4)_6]$.

9. AlignIt σ_{ideal} values in comparative scale of ten-vertex polyhedra

AlignIt is available for download at:

https://github.com/AndyNano/AlignIt.git

Table 1. Full comparative symmetry deviations σ_{ideal} for idealized ten-vertex polyhedra[a,b]



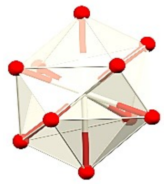
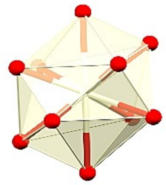
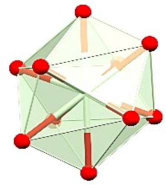
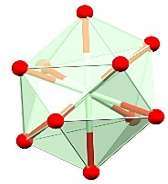
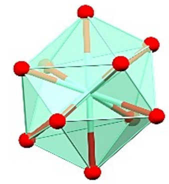
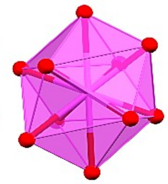
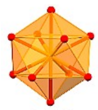
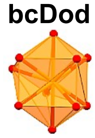
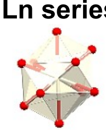
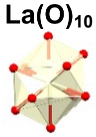
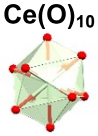
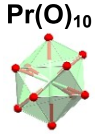
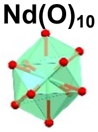
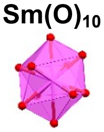
X\Z	bcSAP D_{4d}	bcDod D_2	SDod D_2	PP D_{5h}	PAP D_{5d}	OBPy D_{8h}
bcSAP	0	2.31	7.93	16.45	14.87	16.14
bcDod	2.31	0	10.48	14.95	8.62	14.26
SDod	7.93	10.48	0	10.76	13.97	24.17
PP	16.45	14.96	10.76	0	6.55	22.22
PAP	14.87	8.62	13.97	6.55	0	15.87
OBPy	16.14	14.26	24.17	22.22	15.88	0

[a] Coordinates for the SDod model are reported by Ruiz-Martínez *et al.*[3]. Coordinates for bcSAP, bcDod, PP, PAP and OBPy were created in Mercury (bcSAP and bcDod from description by Al-Karaghouli *et al.* [4,5]). [b] Values in bold are calculated with AlignIt, and values in parenthesis are calculated using SHAPE by Lluenell *et al.*[6]

Calculated $\sigma_{ideal}(Z - X)$ values are above the diagonal and $\sigma_{ideal}(X - Z)$ are below the diagonal.

10. AlignIt σ_{ideal} values in comparative scale of ten-vertex polyhedra[a]

Table S2 σ_{ideal} values calculated with AlignIt with two decimal points

						
Size ratio	**$La(O)_{10}$** **1.0315**	**$Ce(O)_{10}$** **1.0278**	**$Pr(O)_{10}$** **1.0202**	**$Nd(O)_{10}$** **1.0144**	**$Sm(O)_{10}$** **1.0039**	**$Eu(O)_{10}$** **1.0000**
Models	**σ_{ideal}(model - $Ln(O)_{10}$)**					
 **bcSAP**	**1.64** 1.63	**1.68** 1.66	**1.45** 1.44	**1.40** 1.39	**1.22** 1.21	**1.15**
 **bcDod**	**3.77** 3.81	**3.84** 3.86	**5.85** 5.86	**3.57** 3.61	**3.41** 3.46	**5.29**
 **SDod**	**10.11** 10.19	**10.40** 10.54	**7.70** 7.90	**9.93** 10.11	**9.65** 9.86	**7.58**
Ln series	**σ_{ideal}($Ln'(O)_{10}$ – $Ln(O)_{10}$)**					
 **$La(O)_{10}$**	**0**	**0.01**	**3.71**	**0.02**	**0.06**	**3.28**
 **$Ce(O)_{10}$**	0.01	**0**	**3.77**	**0.02**	**0.07**	**3.31**
 **$Pr(O)_{10}$**	3.72	3.78	**0**	**3.41**	**3.14**	**0.04**
 **$Nd(O)_{10}$**	0.02	0.022	3.41	**0**	**0.02**	**2.97**
 **$Sm(O)_{10}$**	0.06	0.07	3.15	0.018	**0**	**2.72**
 **$Eu(O)_{10}$**	3.29	3.34	0.045	3.00	2.74	**0**

11. References

(1) Eriksson, A. K.; Casari, B. M.; Langer, V. Pentapotassium sodium hexasulfatodicerate(III). *Acta Crystallographica Section E* **2003,** *59* (11), i149.

(2) Thomsen, M. S.; Anker, A. S.; Kacenaukaite, L.; Sørensen, T. J. We are Never Ever Getting (back to) Ideal Symmetry: Structure and Luminescence in a Ten-Coordinated Europium(III) Sulfate Crystal *Submitted* **2022**.

(3) Ruiz-Martínez, A.; Alvarez, S. Stereochemistry of Compounds with Coordination Number Ten. *Chemistry – A European Journal* **2009,** *15* (30), 7470.

(4) Al-Karaghouli, A. R.; Wood, J. S. Crystal and molecular structure of trinitratobis(bipyridyl)lanthanum(III). *Inorganic Chemistry* **1972,** *11* (10), 2293.

(5) Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M.et al. Mercury 4.0: from visualization to analysis, design and prediction. *Journal of Applied Crystallography* **2020,** *53* (1), 226.

(6) Llunell, M.; Casanova, D.; Cirera, J.; Alemany, P.; Alvarez, S. SHAPE, version 2.1. *Universitat de Barcelona, Barcelona, Spain* **2013,** *2103*.